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Application of quantitative inline NMR spectroscopy for investigation of a fixed-bed chromatographic reactor process

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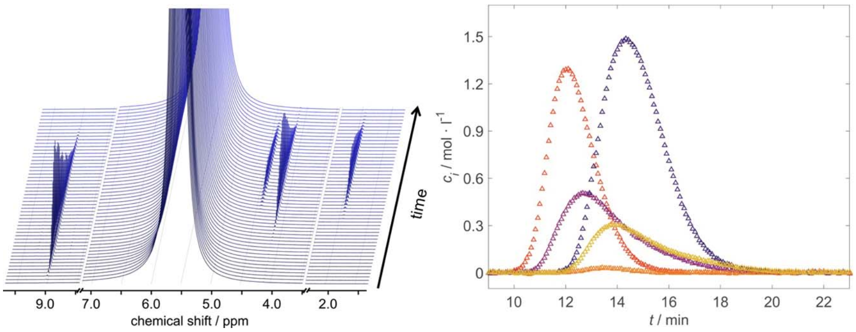
GRAPHICAL ABSTRACT



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ABSTRACT

A Nuclear Magnetic Resonance (NMR) spectroscopy method is presented that facilitates inline analysis of dynamic processes. Compared to other commonly used optical inline analysis methods, NMR spectroscopy has the advantage that it can resolve different species in complex multicomponent mixtures. An inline NMR spectroscopy method was optimized to enable analysis with high temporal resolution. The method was applied to study the dynamic behavior of a fixed-bed chromatographic reactor (FBCR) by monitoring the composition at the reactor outlet.

The heterogeneously catalyzed hydrolysis reactions of methyl acetate and methyl formate were chosen as test systems. The influence of different process parameters such as the concentration of reactants, reactor temperature and flow rate of the mobile phase (water) were systematically studied with the presented method. The concentration profiles of the different reactants and products could be determined accurately even though the two hydrolysis reactions proceeded simultaneously in the FBCR and the concentration profiles of the different species overlapped strongly. The measured concentration profiles are in good agreement with additional RI measurements which, however, do not facilitate a component specific analysis.

The accurate measurement of the concentration profiles enables to study the interaction of reaction and separation in the FBCR. At low concentrations of the reactants the measured concentration profiles agree well with predictions based on a model of the FBCR developed in previous works. At higher concentrations, however, the comparison of the predictions and experimental results reveals deficits in the model. The results demonstrate

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that the presented inline NMR spectroscopy method is a valuable tool to gain insights into complex dynamic processes and to gather accurate experimental data that is essential for the development of reliable process models.

1. Introduction

The startup and shutdown of chemical processes, or periodic operation of reactors [1], adsorbers [2,3] or distillation columns [4] are just a few examples of dynamic processes in the chemical industry. Advanced experimental techniques are needed to study such dynamic processes. These experimental studies are required to gather information concerning the operation and design of the process. In particular, they are needed to develop and parametrize models that can reliably predict the behavior of the process and that can be applied to scale-up and to optimize the process. To gather sufficient information on reactions and mass transfer, taking place during the process, it is often necessary to monitor the composition of feed and product streams with an high temporal resolution over a long period of time.

The fixed-bed chromatographic reactor (FBCR) is a good example to illustrate the analytical challenges that emerge when a highly dynamic process is experimentally investigated. FBCR is a hybrid process that combines reaction and separation in one apparatus. This combination has various potential advantages compared to conventional processes, in which the reaction and the separation of the reactants and products is carried out sequentially using different apparatuses. Especially, if the conversion of the reaction is limited by chemical equilibrium, reactive separation processes can be beneficial [5]. Chromatography is a very versatile and highly selective separation technique. Thus it is widely applied for analysis and purification in the food and pharmaceutical industries, and for the production of fine chemicals [6,7]. In a chromatographic process the separation of the species is based on their different adsorptivities to an adsorbent (the so-called stationary phase) that is immobilized in the chromatographic column. In a FBCR, the adsorbent is additionally catalytically active so that reaction and separation of the different species occur simultaneously in the column. Hence, high conversions of the reactants and good separation of the products can be obtained in a FBCR. Despite these advantages, reactive chromatography has not been widely adopted mainly because of its complexity and the resulting difficulties in designing and optimizing this process. Therefore, analytical methods are required that enable detailed experimental investigations of the different processes taking place in a FBCR.

In a typical reactive chromatography experiment, a fixed amount of reactants is injected into the stationary phase passing through the FBCR, and the outlet of the reactor is analyzed i.e. the chromatogram is recorded. Repeated sampling of the reactor outlet and offline analysis of the collected samples using e.g. gas chromatography [8–11] is only possible if the temporal change of the composition of the reactor outlet is slow so that a sampling rate of 1–2 samples per minute, which is feasible for offline analysis, is sufficient. Thus, to study highly dynamic processes, offline analysis methods are often not applicable, and inline analysis methods must be used. In this case, the reactor outlet is directly connected with a detector that is equipped with a flow cell so that the product stream leaving the reactor passes through that flow cell where its composition can be analyzed.

Refractive index detectors (RID) are often used for inline analysis [12–16,11]. Furthermore, the application of UV/Vis [17,13,18], IR [19] or Raman spectroscopy [20,21], either as single detection method or in combination with RID or offline GC for validation, is reported in literature. RI and UV/Vis detectors have several advantages: they have a high data acquisition rate (typically more than one data acquisition per second), they are sensitive and they are easy to use. The main drawback of these detectors is that the composition of multi-component mixtures cannot generally be obtained from the acquired signal. Hence, important information on the performance of the investigated process such as the conversion of the reactants, the yield of the different products or the product purity are not directly quantifiable from the measured chromatograms. Only if the species are well separated in the FBCR, so that the product stream consists effectively only of a binary mixture of an analyte and the mobile phase (e.g. water), the concentration profile of the analyte (that is the concentration of an analyte as function of time) can be determined from the RID measurements or the UV/Vis signal. If the species are not well separated and the measured signal is a superposition of the contribution of the different species, only model based data evaluation is possible [12]. In this case, first the concentration profiles in the reactor outlet are predicted by a process model and then the simulated concentration profiles are translated into the measurement signals using a calibration model of the analysis method. However, the validation of the process model by comparison of RID or UV/Vis signal with the simulation results is often ambiguous. That means the signal predicted by the process model is the same even if different values of the model parameters are applied. All in all, these disadvantages clearly limit the application of RI or UV/Vis detectors for studying these complex dynamic processes.

Compared to RI and UV/Vis detectors, ones based on IR or Raman spectroscopy have the advantage that different species can be distinguished in the acquired signals. The resulting peaks in the IR or Raman spectrum associated to the different species, however, are often overlapped [22,23]. The overlapping of peaks hinders the quantitative analysis of the spectrum and often requires extensive and tedious calibration procedures for all components within a wide concentration range.

Therefore, a method based on NMR spectroscopy is developed in this work that facilitates inline analysis of dynamic processes. NMR spectroscopy has the great advantage that it can often resolve different species in multi-component mixtures even though they are chemically similar. Moreover, little or no effort on calibration is needed to get quantitative results (that is the composition of the investigated mixture) from the acquired NMR spectra [24]. For that reason, quantitative NMR spectroscopy has manifoldly been used for example for monitoring reactions in a variety of different set-ups [25–33].

Coupling of NMR spectroscopy with liquid chromatography (LC) is a well-established technique [34–38]. LC and NMR spectroscopy, however, are not coupled to study the dynamic processes occurring in the LC column but to separate different species from a multi-component mixture and to elucidate successively the structure of the species by NMR spectroscopy methods. Often the flow through the LC column is even stopped when the species of interest has reached the NMR flow cell so that elaborate and time-consuming NMR pulse sequences can be applied. Hence, the application of NMR spectroscopy for studying dynamic processes such as FBCR requires different methods than the well-established methods used for LC-NMR applications.

Compared to the other analytical methods discussed above, NMR spectroscopy has the drawback that its sensitivity (that is the limit of detection) and its signal acquisition rate is typically lower. An enhancement of the signal acquisition rate is in most cases only possible at the cost of sensitivity. Furthermore, a short mean residence time with a narrow residence time distribution from the investigated process stream to the NMR flow cell is important. In that way, the influence of the detector on the concentration profiles is minimized and the measured concentration profiles are as close as possible to the concentration profiles of the investigated process stream. For this reason, an NMR detector was optimized in this work so that a good compromise between sensitivity, temporal resolution and residence time distribution was found.